Improvement of SEM-SXES analysis for beam sensitive materials by using cooling stage



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Introduction

Soft X-Ray Emission Spectrometer (SXES), which can be installed on SEM and EPMA (Electron probe microanalyzer), is a useful method for chemical state analysis by detecting the energy state of valence electrons. In particular, since SXES can detect low-energy characteristic X-rays such as lithium (Li) K-line and analyze the chemical state, it is expected to be a chemical state analysis method of Lithium Ion secondary Battery (LIB) materials in a charged state. Field Emission-SEM equipped with SXES enables us to obtain chemical state information in the vicinity of the bulk top surface by low-kV analysis.⁽¹⁾ However, it is known that the irradiation of an electron beam causes a change in the chemical state of the beamsensitive materials such as lithium compounds during the observation.⁽²⁾

This study shows the improvement of chemical state analysis for beam-sensitive materials using the SEM-SXES system with a cooling stage.

SXES Analysis for PTFE using cooling stage

SXES analysis for PTFE at RT and -100 °C cooling, was performed at an accelerating voltage of 3 kV and a probe current of 20 nA, using SS-94040SXSER. In the time-resolved SXES analysis of PTFE at RT performed every 10 seconds from 0 to 200 seconds, the intensity of F spectrum changes in response to the irradiation time. This demonstrates that PTFE is defluorinated and carbonized as the dose of the electron beam increases. On the other hands, as a result of SXES analysis with -100°C cooling, no big change with the passage of time was confirmed in the SXES spectrum which was timeresolved every 10 seconds from 0 to 200 seconds. This result leads the possibility of applying the SXES analysis for polymer material by using the cooling stage.



Instrument and method

The Schottky FE-SEM, JSM-IT800(JEOL), combined with the SXES, SS-94000SXES or SS-94040SXSER (JEOL), and cooling stage C1003 (Gatan, Inc.), was used to examine Lithium Sulfide (Li₂S) reagent for the solid electrolyte of LIB, PTFE and solid state battery to confirm the reduction effect of specimen degradation during electron beam irradiation using a specimen cooling stage. To prevent deterioration of the specimen due to atmospheric exposure, the specimen was transferred to the SEM-SXES system using a transfer vessel for air isolation. The changes in the chemical state of specimens were confirmed by visualization of time-resolved SXES analysis.⁽²⁾



FE-SEM : JSM-IT800 (JEOL)

Possible to provide large probe current for SXES analysis even at low accelerating voltages, with optimized electron probe.

SXES : SS-94000SXES (JEOL)

Energy resolution 0.3 eV(AI-L spectrum measured @73 eV) Acquisition energy range: 50-170 eV (Grating: JS50XL), 70-210 eV (Grating: JS200N)

- SS-94040SXSER (JEOL)
- Energy resolution 1.2 eV (Zr-M ζ FWHM), 5.0 eV (Fe-L α FWHM)
- Acquisition energy range: 100-400 eV (Grating: JS-300N), 350-2300 eV (Grating: JS2000)

Cooling Stage: C1003 (Gatan, Inc.)

-100°C cooling



SXES analysis for 50% charged Si negative electrode in solid state battery

SXES mapping analysis for cross section of 50% charged Si negative electrode in solid state battery

Operating temperature: -185 °C to 400 °C

Reduction of sample degradation during electron beam irradiation by using specimen cooling stage



-100°C cooling



Backscattered Electron (BSE) image

Screw type exchange rod



BSE image

After

Before

Analytical

(half cell)

Reference electrode (In-Li alloy) $Li_2S-P_2S_5-Lil$ (LPSI) Solid electrolyte Si negative electrode laver

LPSI solid electrolyte prepared by liquid-phase syntheses (3) and Si particles were used for negative electrode. A half-cell was prepared using this negative electrode and charged at 50% of the theoretical capacitance value of Si.

SXES Mapping result



at -120 °C cooling, was performed at an accelerating voltage of 5 kV and a probe current of 50 nA, using SS-94000SXES. It can be seen that SXES mapping can be performed stably without damaging or degradation the sample such as formation of Li deposition. A correlation between the Li intensity and the Si intensity and the BSE image contrast can be seen, and the distribution of the Li intensity in the grain, that is, the difference in the charged state, can be confirmed. Spectral extraction from the SXES map reveals that the intensity ratios of Li and Si differ in each area and that the chemical states differ as seen in the spectral shapes. The difference in chemical states during the charging process inside the Si particle could be revealed by using cooling stage and SXES analysis.

50% Charged Si negative electrode



5 kV, 50 nA, 80 x 60 point, Dwell time : 1.5 sec/point

5 µm



Cross-sectioned by an Ar ion beam using a COOLING CROSS SECTION POLISHER[™] (CP)

Toyohashi Univ. of Technology

(JEOL, IB-19520CCP) under high vacuum and cooling conditions.

Specimen courtesy : Professor Atsunori Matsuda

Dept. of Electrical and Electronic Information Engineering,

BSE image



SXES point analysis for Li₂S at RT and -120 °C cooling, was performed at an accelerating voltage of 3 kV and a probe current of 20 nA, using SS-94000SXES. When Li₂S at RT is continuously irradiated with an electron beam for 450 seconds, formation of deposition on the specimen surface can be confirmed in the BSE image. In the timeresolved SXES analysis performed every 15 seconds from 0 to 450 seconds, the Li spectrum changes in response to the irradiation time. This demonstrates that Li is metallized as the dose of the electron beam increases. As a result of SXES point analysis with -100°C cooling, there was no change in contrast in the BSE image. It can be seen that no precipitation has occurred on the surface of Li₂S after performing SXES analysis with an acquisition time of 450 seconds. Even in the SXES spectrum which was time-resolved every 15 seconds from 0 to 450 seconds, no spectral big change with the passage of time was confirmed. Comparing the SXES results obtained at RT and at -100°C, it can be seen that the Li K spectrum derived from metallic lithium was not detected and the Li K spectrum derived from Li₂S was obtained by cooling at -100 °C.

Comparison of SXES whole spectra: RT and -100°C cooling

■5 um





Summary

The improvement of chemical state analysis using the SEM-SXES with a cooling stage for beam-sensitive materials was confirmed from this study. In particular, the application of this method to the analysis of battery materials can be expected, such as a comprehensive analysis in which TEM lamella is prepared at the same location with FIB after mapping by SEM-SXES and analyzed with TEM.

References

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